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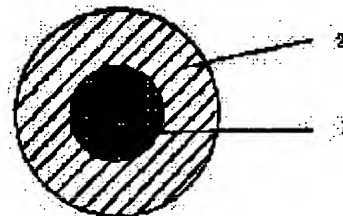
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(54) COATING MATERIAL AND ELECTRIC WIRE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain both a coating material having various characteristics such as tensile properties, wear resistance, flexibility, flame retardance, freeze resistance, etc., required as properties of a coating material for internal wiring of electronic device and automobile, core wire of optical fiber, optical fiber cord, etc., having no elution of heavy metal compound, emitting neither a large amount of smoke nor a corrosive gas, and to produce electric wire coated with the coating material.

SOLUTION: This coating material is obtained by blending 100 pts.wt. of a resin composition comprising (a) ≥20wt.% of a polypropylene based resin and (b) 40-80wt.% of a styrene-based thermoplastic elastomer composed of a polystyrene as a hard segment and a hydrogenated substance of a (co)polymer of butadiene and/or isoprene with (c) 30-70 pts.wt. of ammonium polyphosphate-based flame-retardant and (d) 80-120 pts.wt. of a metal hydride. The objective electric wire is obtained by coating the outer periphery of a conductive material 1 with a coating layer 2 of the coating material.



no tensile strength
fiber layer

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elastomers which have the hydride of a butadiene and/or an isoprene (**) polymer as a soft segment The covering material characterized by coming to blend the mixture (D) 30 of a polyphosphoric acid ammonium system flame retarder and a metal hydrate, - 120 weight section, (3) (1) to which the aforementioned resinous principle (A) is characterized by containing an ethylene system copolymer (a3) in 30 or less % of the weight of the domain, or covering material given in (2) terms, And the electrical wire characterized by covering the periphery of a conductor with covering material (4), (1), (2), or given in (3) terms is offered.

[0006]

[Gestalt of implementation of invention] Hereafter, this invention is explained in detail. First, each component which constitutes the covering material of this invention is explained.

(a1) As a polypropylene resin used in a polypropylene resin this invention A polypropylene homopolymer, an ethylene propylene block copolymer, An ethylene propylene random copolymer, a propylene and 1-butene block copolymer, A propylene and 1-butene random copolymer, a propylene and 4-methyl pentene-1 block copolymer, It can use combining one sort of the resin chosen out of a propylene and 4-methyl pentene-1 random copolymer, a propylene and 1-hexene block copolymer, a propylene, 1-hexene random copolymer, etc., or two sorts or more. Among these, an ethylene propylene block copolymer and an ethylene propylene random copolymer are desirable. The melt flow rate (MFR) of an ethylene propylene block copolymer and an ethylene propylene random copolymer has the desirable thing of the domain for 0.5-15g / 10 minutes (load 2.16kgf, temperature of 230 degrees C).

[0007] (a2) The styrene thermoplastic elastomer used in a styrene thermoplastic elastomer this invention has polystyrene as a hard-segment, and has the hydride of a butadiene and/or an isoprene (**) polymer as a soft segment. This hydrogenates the latter copolymer of a block which consists of the block B which consists of the homopolymers or those copolymers of block segment A which consists of polystyrene, and a butadiene or an isoprene. As block A, polystyrene, a poly-o-methyl styrene, a poly-m-methyl styrene, a poly-p-methyl styrene, a poly-alpha methyl styrene, a poly-beta-methyl styrene, poly-dimethyl styrene, polytrimethyl styrene, etc. are mentioned, and a polybutadiene, a polyisoprene, a butadiene isoprene copolymer, etc. are mentioned as block B.

[0008] The styrene thermoplastic elastomer used for this invention is possible also for use of the A-B-B' type triblock copolymer using block B' to which the amount of vinyl combination of block B was reduced in order to raise a fluidity besides an A-B-A type triblock copolymer, and it can also combine two or more sorts of these. The hydride of these block copolymers has that desirable by which block A is hardly hydrogenated but block B and B' is hydrogenated alternatively. As such a thing, "KRATON" (a tradename, SHELL company make), "die *****" (a tradename, Japan Synthetic Rubber Co., Ltd. make), etc. are marketed.

[0009] In order to give fire retardancy, a polyphosphoric acid ammonium system flame retarder and/or a metal hydrate are blended with the covering material of this invention.

It sets to a polyphosphoric acid ammonium system flame-retarder this invention, and is tris as a polyphosphoric acid ammonium system flame retarder (the Lynn system flame retarder). -(2-hydroxyethyl)- The polyphosphoric acid ammonium containing nitrogen inclusion compounds, such as isocyanurate, a melamine, and a polyphosphoric acid amide, is used. As such a thing, "Hostaflam AP745" (a tradename, product made from HOECHST), "Sumisafe PM" (a tradename, Sumitomo Chemical Co., Ltd. make), etc. are marketed.

[0010] As a metal hydrate and a metal hydrate, it can use combining one sort of the inorganic compound which has a hydroxyl group or water of crystallization, such as an aluminum hydroxide, a magnesium hydroxide, a hydration aluminum silicate, a hydration magnesium silicate, a basic magnesium carbonate, and a hydrotalcite, or two sorts or more. Among these, a magnesium hydroxide is desirable and what performed especially surface treatment is desirable. As such a thing, commercial elegance, such as "***** 5, 5A, 5B, 5E, and 5J" (a tradename, consonance chemistry company make), can be used.

[0011] Moreover, in order to raise the flame-resisting effect of these polyphosphoric acid ammonium system flame retarder and a metal hydrate, it is also possible to blend quartz-glass fillers, such as silicone compounds, such as "SFR-100" (a tradename, product made from GENERAL ELECTRIC), and "a crystallite, fuse Rex" (a tradename, product made from **** Co.). In order to improve a fall of the mechanical characteristic in the case of using a metal hydrate, a quartz-glass filler, etc., you may use the denaturation polyolefine which denaturalized polyolefines, such as "N polymer" (a tradename, the Nippon Oil chemistry company make), with a unsaturated carboxylic acid or its derivative.

[0012] (a3) The covering material of an ethylene system copolymer this invention In the combination with a polyphosphoric acid ammonium system flame retarder and a metal hydrate Fuming is reduced or it aims at raising fire retardancy. Ethylene and a vinyl acetate copolymer (EVA), Ethylene and an ethyl-acrylate copolymer (EEA), ethylene and a methyl-acrylate copolymer (EMA), Ethylene system copolymers (a3), such as ethylene and a methyl-methacrylate copolymer (EMMA), ethylene and an acrylic-acid copolymer (EAA), and ethylene, a methacrylic-acid copolymer (EMAA), can be blended in less than 30% of the weight of the domain into a resinous principle. EVA and EEA are desirable among these ethylene system copolymers. MFR of an ethylene system copolymer has the desirable thing of the domain for 0.5-10g / 10 minutes (load 2.16kgf, temperature of 190 degrees C).

[0013] Next, each blending ratio of coal of the polypropylene resin (a1) in the covering material of this invention, a styrene thermoplastic elastomer (a2), an ethylene system copolymer (a3), a polyphosphoric acid ammonium system flame retarder, and a metal hydrate is explained. The rate of a polypropylene resin (a1) is 20% of the weight or more of the total amount of the resinous principle which consists of a resinous principle (A), i.e., a polypropylene resin, a styrene thermoplastic elastomer, an ethylene system copolymer, etc., and is desirable. [of 25 - 50 % of the weight] When this rate is 20 % of the weight or more, since mechanical characteristics, such as abrasion resistance and a **** property, and thermal resistance are good, it is suitable as covering material, such as an internal wiring and optical fiber core wire of electronic equipment or an automobile, and a code.

[0016] It becomes possible to make fuming and the fire retardancy of covering material improve more of combination of an ethylene system copolymer (a3) by blending this. However, it is desirable still desirable that it is less than 30 % of the weight in a resinous principle (A), and the rate is 5 - 25 % of the weight. If it becomes 30% of the weight or more, a heat-resistant fall of covering material may start. Furthermore, in the covering material of this invention, in order to raise the fire retardancy, you may add carbon black, red phosphorus, etc. Moreover, you may add an antioxidant, an ultraviolet ray absorbent, a copper inhibitor, a dispersant, a pigment, etc. if needed.

[0018] Although covered with the covering material of this invention, the example of structure is shown in drawing 1 -3. Drawing 1 is the cross section of one example of the electrical wire of this invention with which the covering material of this invention is prepared in the periphery of the conductor 1 which consists of solid wire or a stranded wire as an insulating layer 2. Drawing 2 is the cross section of other examples of the electrical wire of this invention with which an insulating layer 2 and the cutoff layer 3 are formed in the periphery of a conductor 1 at this order, and the covering material of this invention is prepared in the periphery as a protection layer (sheath) 4. Drawing 3 is the cross section of an example of the optical fiber code which formed the protection layer 6 which becomes the periphery of optical fiber core wire or the optical fiber code 5 from the covering material of this invention. Drawing 4 is the cross section of an example of the optical fiber code which formed the protection layer 6 which attaches the tensile-strength field 7 to the periphery of the optical fiber core wire 5, and becomes the periphery from the covering material of this invention in the optical fiber code of drawing 3 .

[Example] Hereafter, an example and the example of a comparison explain this invention still in detail.

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the minimum abrasion-resistance value (mm) of each electrical wire based on the wear tape method of an antifriction examination of automobile specification (JASO D 608-92). Weight was set to 450gves and the minimum abrasion-resistance value considered the thing 457mm or more as success (O).

[0020] It is [fire retardancy] JIS about each electrical wire. It evaluated according to C3005. **** time was made into 15 seconds and measured time until the flame of electrical wire after removing the flame of a burner disappears automatically. Fuming created the heat press sheet of each covering material, and evaluated it by NBS fuming examination. a ratio -- optical density made [125 or less thing] ** and 175 or more things x for O and the thing of 125-175 The increase in a loss at the time of a heating deformation examination of insulated wire, the examination with a low-temperature volume, and the thermo-cycle examination after optical fiber core-wire covering estimated thermal resistance and cold resistance. About a heating deformation examination of insulated wire, it is JIS. It evaluated according to C3005. The test temperature was set it as 120 degrees C, the load was set to 306gves, and the thing of 30% or less of reduction of areas was considered as success (O). After the examination with a low-temperature volume left insulated wire in the -40-degree C cryostat for 1 hour, it twisted around the mandrel of the diameter of self in the cryostat, and investigated the existence of the crack in an insulator. The case of O and crack **** was made into x for the case where he has no crack. As for the thermo-cycle examination, transmission loss with a measurement wavelength [in / in the increase with a measurement wavelength / in a four-cycle deed and a 0-80-degree C elevated-temperature field / of 1.55 micrometers in transmission loss / a heat-resistant O and a -20-0-degree C low-temperature field for a thing 0.05dB /km / or less] of 1.55 micrometers made the thing 2.0dB [km] or less cold-resistant O at the temperature of -20-80 degrees C. [0021] About extrusion-molding workability, the extrusion covering equipment of 35mm of the diameters of a cylinder was used, it was 200 degrees C in 180 degrees C of cylinder temperatures, and crosshead temperature, and when extrusion covering was carried out on the annealed copper wire of 0.80mm of the diameters of a conductor, the extrusion covering speed from which the insulated wire with a good appearance is obtained made the thing of the following x for the above thing by O and 50m/by 50m/. [0022] In addition, each component shown in Tables 1-4 used the following.

(01) Ube Industries, Ltd. make Ethylene propylene random-copolymer;MFR5g / 10 minutes (230 degrees C, 2.16kgf)
 Tradename RF338A(02) Ube Industries, Ltd. make Ethylene propylene block-copolymer;MFR3g / 10 minutes (230 degrees C, 2.16kgf)
 Tradename J903HK(03) SHELL company make Styrene thermoplastic elastomer;MFR10g / 10 minutes (200 degrees C, 5kgf)
 Tradename Clayton G1652 (04) Japan Synthetic Rubber Co., Ltd. make Styrene thermoplastic elastomer;MFR3.5g / 10 minutes (230 degrees C, 2.16kgf)
 Tradename Die ***** 1320P(05) Mitsui DU-PONT-DE-NEMOURS poly chemical company make Ethylene and vinyl acetate copolymer;MFR1.0g / 10 minutes (190 degrees C, 2.16kgf)
 Vinyl acetate content 28wt% tradename Eve FREX EV-270[0023] (06) The Mitsui DU-PONT-DE-NEMOURS poly chemical company make Ethylene and ethyl-acrylate copolymer;MFR0.5g / 10 minutes (190 degrees C, 2.16kgf)
 Vinyl acetate content 15wt% tradename Eve FREX A-710 (07) Nippon Oil chemistry company make Denaturation polyolefine;MFR1.0g / 10 minutes (190 degrees C, 2.16kgf)
 tradename N polymer L6100M(08) Japan Synthetic Rubber Co., Ltd. make ethylene-propylene rubber; tradename EP01P(09) Riken Vinyl Industry Co., Ltd. make Polyvinyl chloride compound; tradename IG-5071 (10) Sumitomo Chemical Co., Ltd. make Polyphosphoric acid ammonium system flame-retarder A; tradename Product made from Sumisafe PM(11) HOECHST polyphosphoric acid ammonium system flame-retarder B; tradename Hostaflam AP745 (12) consonance chemical-industry company make magnesium-hydroxide; tradename ***** 5A(13) GENERAL Product made from ELECTRIC silicone; tradename SFR- pen ***** chill-tetrakis made from 100 (14) CIBA-GEIGY [-- 3 - (3, 5-G t-butyl-4-hydroxyphenyl) propionate; tradename IRGANOX1010 [0024]
 [Table 1]

表1

実施例		1	2	3	4	5	6	7
配合量 入重量部 V	R-PP (01)	55	25	40	40	40	40	
	B-PP (02)							40
	SEBS (03)							
	HSBR (04)	45	75	60	60	60	60	60
	EVA (05)							
	EEA (06)							
	MAH-G-PE (07)							
	EPR (08)							
	PVC (09)							
	ポリメチルメタクリレート系樹脂A (10)	50	50	35	65			50
	ポリメチルメタクリレート系樹脂B (11)							
	酸化マグネシア (12)					90	110	
	シリコン (13)							
	顔料 (14)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
特性	引張特性							
	引張強度 (MPa)	20	15	18	16	14	12	20
	伸び (%)	800	1000	850	800	800	500	700
	耐摩耗性	○	○	○	○	○	○	○
	難燃性	4~12	16~24	15~21	8~12	18~24	10~12	10~14
	発煙性	△	○	○	△	○	○	△
	耐熱性							
	絶縁電線	○	○	○	○	○	○	○
	光ファイバ心線	○	○	○	○	○	○	○
	耐寒性							
	絶縁電線	○	○	○	○	○	○	○
	光ファイバ心線	○	○	○	○	○	○	○
	押出成形加工性	○	○	○	○	○	○	○

[0025]

[Table 2]

表2

実施例		8	9	10	11	12	13	14	15
配合量 入重量部 V	R-PP (01)	40	40	40	25	25	40	35	40
	B-PP (02)								
	SEBS (03)	60	30						
	HSBR (04)		30	60	50	50	60	60	60
	EVA (05)				25				
	EEA (06)					25			
	MAH-G-PE (07)							5	
	EPR (08)								
	PVC (09)								
	ポリメチルメタクリレート系樹脂A (10)	50	50		50	50	45		50
	ポリメチルメタクリレート系樹脂B (11)			50					
	酸化マグネシア (12)							100	50
	シリコン (13)						5		
	顔料 (14)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
特性	引張特性								
	引張強度 (MPa)	27	25	16	15	15	20	15	15
	伸び (%)	550	650	800	700	700	750	550	600
	耐摩耗性	○	○	○	○	○	○	○	○
	難燃性	12~18	10~14	2~4	2~6	2~4	3~6	12~20	12~22
	発煙性	△	△	○	○	○	○	○	○
	耐熱性								
	絶縁電線	○	○	○	○	○	○	○	○
	光ファイバ心線	○	○	○	○	○	○	○	○
	耐寒性								
	絶縁電線	○	○	○	○	○	○	○	○
	光ファイバ心線	○	○	○	○	○	○	○	○
	押出成形加工性	○	○	○	○	○	○	○	○

[0026]

[Table 3]

表3

比較例		1	2	3	4	5	6	7
配合量 ハ重 量部 V	R-PP (01)		100		65	15	40	40
	B-PP (02)							
	SEBS (03)							
	PSBR (04)				35	85		60
	EVA (05)			95				
	EEA (06)							
	MAH-G-PE (07)			5				
	EPR (08)						60	
	PVC (09)	100						
	ポリブチレン系樹脂A (10)				50	50	50	25
	ポリブチレン系樹脂B (11)							
	塩化マグネシウム (12)		100	100				
	シリコン (13)							
	顔料 (14)		0.5	0.5	0.5	0.5	0.5	0.5
特性	引張特性							
	引張強度 (MPa)	18	22	10	24	9	10	18
	伸び (%)	300	550	400	650	1000	500	800
	耐摩耗性	○	○	×	○	○	○	○
	難燃性	1~3	14~24	10~16	4~8	20~30	12~18	25~40
	発煙性	×	○	○	△	○	△	○
	耐熱性							
	絶縁電線	○	○	×	○	○	×	○
	光ファイバ心線	○	○	○	○	○	○	○
	耐寒性							
	絶縁電線	○	×	○	○	○	×	○
	光ファイバ心線	○	×	○	×	○	○	○
	押出成形加工性	○	○	○	○	×	○	○

[0027]

[Table 4]

表 4

比較例		8	9	10	11
配 合 量 入 量 部 V	R-PP (01)	40	40	40	15
	B-PP (02)				
	SEBS (03)				
	HSBR (04)	60	60	60	50
	EVA (05)				35
	EEA (06)				
	MAH-G-PE (07)				
	EPR (08)				
	PVC (09)				
	ポリプロピレン系樹脂A (10)	75			
	ポリプロピレン系樹脂B (11)				
	炭化7% 樹脂 (12)		70	130	
	シリコン (13)				
	炭化樹脂 (14)	0.5	0.5	0.5	0.5
特 性	引張特性				
	引張強度 (MPa)	15	18	8	10
	伸び (%)	750	650	250	500
	耐摩耗性	○	○	×	○
	難燃性	5~9	28~40	10~14	1~4
	免煙性	×	○	○	○
	耐熱性				
	絶縁電線	○	○	○	×
	光ファイバ心線	○	○	○	○
	耐寒性				
	絶縁電線	○	○	○	○
	光ファイバ心線	○	○	○	○
	押出成形加工性	○	○	○	○

[0028] The result of Tables 1-4 shows the following things. Although the example 1 of a comparison is an example which used the polyvinyl chloride compound as covering material and it is the material excellent in various properties, there is a problem generate a lot of smoke and corrosive gases at the time of the combustion. It is the purpose that this invention offers the alternate material of this polyvinyl chloride compound. The example 2 of a comparison is an example which used only the ethylene propylene random copolymer as a base polymer. Although this thing is the non halogen fire retarding material excellent in the mechanical strength, when it considers as a wire-covering material, when [in low temperature] a problem is that it is good in **** and it considers as the covering material of optical fiber core wire, there is a problem that transmission loss increases remarkably, in a low-temperature field. It is the example for which the example 3 of a comparison used ethylene and the vinyl acetate copolymer as a base polymer, and used the magnesium hydroxide as a flame retarder. Although the denaturation polyolefine is blended for the purpose of raising the compatibility of a base polymer and a metal hydrate, there is a problem that mechanical characteristics, such as a **** property and abrasion resistance, are low. Moreover, depending on a base polymer, thermal resistance is low.

[0029] The examples 4 and 5 of a comparison make the loadings of a styrene thermoplastic elastomer out of range [this invention]. Although tensile strength improves from contrast of the example 4 of a comparison, and the example 1 when the loadings of a styrene thermoplastic elastomer are made into less than 40% of the weight of a resinous principle, it turns out that the increase in the transmission loss in a low-temperature field is not improved. Moreover, it turns out that a fall of **** luminous intensity and a fall of extrusion-molding workability pose a problem from contrast of the example 5 of a comparison, and the example 2 on the other hand although the increase in transmission loss [field / low-temperature] when the loadings of a styrene thermoplastic elastomer surpass 80 % of the weight is improved.

[0030] The example 6 of a comparison is an example which did not blend a styrene thermoplastic elastomer but blended ethylene-propylene rubber. A problem is in the thermal resistance and cold resistance in a fall and insulated wire of tensile strength so that it may understand by the contrast with examples 3 and 4 etc.

[0031] The examples 7 and 8 of a comparison make the loadings of a polyphosphoric acid ammonium system flame retarder out of range [this invention]. Since self-***** in a combustion test was extended when the loadings of a polyphosphoric acid ammonium system flame retarder were made under into 30 weight section to the resinous principle 100 weight section so that it might understand by the comparison with examples 3 and 4, when a problem arises in fire retardancy and 70 weight section is surpassed, fuming poses a problem and it does not change at all with the polyvinyl chloride compound of the example 1 of a comparison which has a problem about this point.

[0032] The examples 9 and 10 of a comparison are examples at the time of using a metal hydrate in the amount of this invention

out of range as a flame retarder. The contrast with examples 5 and 6 shows that a problem arises in fire retardancy to the resinous principle 100 weight section when the loadings of a metal hydrate are under 80 weight section, and the problem to which mechanical characteristics, such as a **** property and abrasion resistance, fall arises in surpassing 120 weight section. The example 11 of a comparison is an example which had loadings [good] for the ethylene system copolymer for 30 % of the weight in a resinous principle. While fire retardancy will improve when the loadings of an ethylene system copolymer increase if it contrasts with an example 11, it turns out that a **** property and thermal resistance fall.

[0033] An example 7 is an example which used the ethylene propylene block copolymer as a polypropylene resin. It turns out that a block copolymer can be used like a random copolymer. A block copolymer is desirable when thinking the thermal resistance of covering material as important. An example 8 is an example which used the A-B-A type thing as a styrene thermoplastic elastomer. Although extrusion-molding workability falls a little as compared with the A-B-B' type thing currently used in other examples, not the level that poses a problem as covering material but tensile strength improves. An example 9 can have the outstanding fabricating-operation nature which an A-B-A and A-B-B' high mechanical-characteristic [which is the example which used two of types and an A-B-A type has] and A-B-B' type has as a styrene thermoplastic elastomer.

[0034] Although an example 10 is an example which used the polyphosphoric acid ammonium system flame retarder from which the nitrogen inclusion compound contained is different, a property top problem is not seen. An example 13 is an example which used together the polyphosphoric acid ammonium system flame retarder and the silicone compound. Use of a silicone compound shows that the fire retardancy of the covering material of this invention improves. In the system which uses a metal hydrate as a flame retarder, an example 14 is an example which blended the denaturation polyolefine, and combination of a denaturation polyolefine is also possible for it for the purpose of raising the compatibility of a base polymer and a metal hydrate.

[0035]

[Effect of the invention] The covering material of this invention as a polypropylene resin (a1) and a hard segment Polystyrene, The resinous principle which comes to contain the styrene thermoplastic elastomer (a2) which has the hydride of a butadiene and/or an isoprene (**) polymer as a soft segment (A), And it comes to blend the mixture (D) of a polyphosphoric acid ammonium system flame-retarder (B) metal hydrate (C), or a polyphosphoric acid ammonium system flame retarder and a metal hydrate by specific proportion. The **** property demanded when used as covering material, such as an internal wiring and optical fiber core wire of electronic equipment or an automobile, and an optical fiber code There are abrasion resistance and the outstanding characteristic feature it not only has various properties, such as ****, fire retardancy, and cold resistance, as it is good, but that no occurrence of the elution of a heavy metal compound, a lot of smoke, and a corrosive gas is in discarding these covering material. the former since it has the outstanding thermal resistance especially as an insulating wire-covering material, and a peroxide -- bridge formation and an electron ray -- the use as an alternative of the covering material which was constructing the bridge is possible, and use in a wide range temperature field is more possible than PVC which is the conventional covering material as covering material, such as optical fiber core wire and a code, from having the outstanding thermal resistance and cold resistance Moreover, the electrical wire of this invention fulfills various properties, such as a **** property demanded as an internal wiring of electronic equipment or an automobile, abrasion resistance, C and ****, fire retardancy; and cold resistance, and does not have occurrence of the elution of a heavy metal compound, a lot of smoke, and a corrosive gas in the abandonment.

[Translation done.]